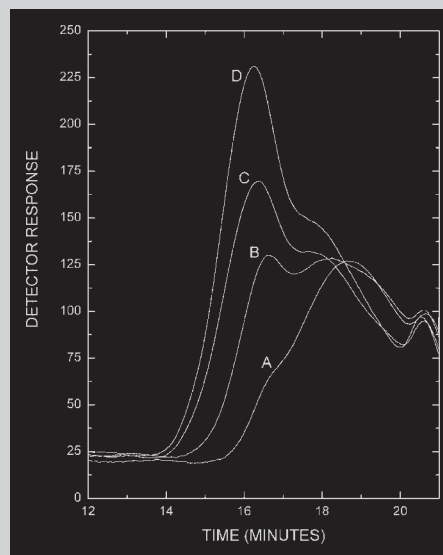


**Summary:** The effects of monomer/starch feed ratios and moisture content during reactive extrusion of starch-polyacrylamide graft copolymers were investigated. Acrylamide/starch ratios ranged from 0.20 to 1.87 at 50% moisture content, while moisture content was increased from 45 to 75% with an acrylamide/starch ratio of 0.33. Average conversion was 86.6% ( $\pm 3.5\%$ ), independent of monomer content, at acrylamide/starch ratios of 0.77 and less. Conversion increased to approximately 95% when the acrylamide/starch ratio exceeded unity. Molecular weight of grafted polyacrylamide increased as the acrylamide/starch ratio increased. Graft efficiency was constant at approximately 75% for monomer/starch ratios of 0.77 or less, and decreased to 52.3% as the monomer/starch ratio increased to 1.87. Higher acrylamide/starch ratios gave more frequent grafts of higher molecular weight. As moisture content decreased from 75 to 45%, conversion and graft content increased from 78 and 14% to 97 and 23%, respectively. Lower moisture content gave fewer grafts of higher molecular weight. Ungrafted polyacrylamide homopolymer increased with monomer/starch ratio and moisture content. These results indicate that graft copolymer properties can be controlled through the monomer/starch ratio and moisture content during reactive extrusion.



Molecular weight distributions of grafted polyacrylamide at different moisture contents during extrusion: A) 75%; B) 65%; C) 55%; D) 45%.

# Reactive Extrusion of Starch-Polyacrylamide Graft Copolymers: Effects of Monomer/Starch Ratio and Moisture Content

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## Introduction

Modified starch-based polymers can be engineered for specific properties by combining starch with synthetic polymers through graft copolymerization.<sup>[1]</sup> Starch-polyacrylamide graft copolymers have received attention given their potential applications in areas such as superabsorbents,<sup>[2,3]</sup> paper-making additives,<sup>[4–7]</sup> drag reduction,<sup>[8]</sup> and textile sizing.<sup>[9]</sup> Methods of preparation typically involve batch processes, often with low conversions and graft efficiencies. Batch processing typically requires long reaction times and

large volumes of water and precipitating solvents. In addition, changing conditions as the reaction proceeds may lead to products with inhomogeneous properties.

We have demonstrated the potential of reactive extrusion as a rapid means of producing starch-polyacrylamide graft copolymers at high efficiencies and reaction times of several minutes.<sup>[10,11]</sup> Using ammonium persulfate as initiator, conversions of 90% or more can be reached with grafting efficiencies of 75% or greater. These results extend the earlier results obtained by Carr et al., who prepared starch-graft-polyacrylamide by reaction extrusion.<sup>[12]</sup> Using ceric

ammonium nitrate as initiator, Carr et al. reported low conversions (10 to 35%) and low grafting efficiency.

This paper presents results on the preparation of starch-graft-polyacrylamide copolymers using a twin-screw extruder in a continuous process. Effects of acrylamide/starch ratio and moisture content during extrusion are reported. Properties including conversion, graft content, graft efficiency, polymer molecular weight, and graft frequency were evaluated.

## Experimental Part

### Materials

Unmodified corn starch (Pure Food Powder, TLNA, Decatur, IL) with approximately 23% amylose was used. Prior to extrusion, starch was sifted through a standard 20 mesh screen to remove lumps. Moisture content of the starch at ambient conditions was 10%. Ammonium persulfate (APS) and hydroquinone were obtained from Sigma Chemical (St. Louis, MO) and used as received. Acrylamide monomer (50% solution) was obtained from Cytec, Inc. and used as received. Deionized water adjusted to pH 8 was used.

### Extrusion

Reactive extrusion was performed using a Werner Pfleiderer ZSK30 co-rotating twin screw extruder (Coperion Corporation, Ramsey, NJ). The barrel was comprised of 14 barrel sections, with a total length/diameter ratio of 44:1. The screw configuration, comprised of several mixing zones and injection ports, has been described elsewhere.<sup>[10]</sup> The screw speed was 150 rpm. Starch was fed into barrel section 1 using a loss-in-weight feeder (AccuRate Inc., Whitewater, WI). The feed throat as cooled with 5 °C water. Moisture content (MC) was adjusted by injecting water into barrel section 2. The initiator (5% solution at pH 8) was injected into barrel sections 2 and 8. Total APS content was 1% based on starch solids, corresponding to one sulfate radical per 70 anhydroglucose units (AGU). The monomer solution was injected into barrel section 4 using a water-cooled injection nozzle. Liquids were pumped using triple-piston liquid metering pumps (Eldex Labs, Napa CA). The temperature profile was 80/90/110/100/80 °C. A die plate with two outlets (4 mm diameter) was used. Total feed rates ranged from 160 g · min<sup>-1</sup> to 210 g · min<sup>-1</sup>.

Extrudate samples were collected at the die after extrusion parameters were stabilized. The extrudate was immediately dispersed into 200 ml of ethanol containing 0.5% hydroquinone in a Waring Blender for 4 min to quench the reaction, followed by steeping overnight. In addition to quenching the reaction, the ethanol solution removed unreacted monomer. Polyacrylamide (PAAm) homopolymer was extracted by stirring 2.5 g graft copolymer in 200 ml of 30/70 ethanol/water (v/v) overnight at room temperature.<sup>[10]</sup> Insoluble solids were collected by filtration and dried. FTIR spectra of samples after extraction (not shown) display the expected amide I (1675 cm<sup>-1</sup>) and amide II (1615 cm<sup>-1</sup>) carbonyl absorption bands from grafted polyacrylamide, consistent with our previous results.<sup>[10]</sup>

### Characterization

Nitrogen contents were measured using a LECO CHN-2000 analyzer using EDTA as a standard. Nitrogen content of AAm is 19.72%. Conversion, graft content and grafting efficiency were calculated by:

$$\text{Conversion} = 100 \times \frac{N_q}{N_f} \quad (1)$$

$$\text{Graft Content} = 100 \times \frac{N_{\text{ext}}}{19.72} \quad (2)$$

$$\text{Graft Efficiency} = 100 \times f \times \frac{N_{\text{ext}}}{N_q} \quad (3)$$

where  $N_q$  is the nitrogen content of the quenched exudates before extraction,  $N_f$  is the theoretical maximum nitrogen content based on feed rates,  $N_{\text{ext}}$  is the nitrogen content of the insoluble graft copolymer after extraction, and  $f$  is the insoluble weight fraction. Grafting efficiency is based on the polymerized monomer, i.e. the ratio of insoluble PAAm to total PAAm.

Starch was removed from the extracted graft copolymer using enzyme hydrolysis prior to size exclusion chromatography (SEC). Approximately 100 mg of graft copolymer was dispersed in 50 ml of deionized water at 80 °C then cooled to below 40 °C. Pullulanase (0.01 ml, 72 U) and  $\alpha$ -amylase (0.1 ml, 300 U) were added, and the mixture was digested overnight in incubating shaker (New Brunswick) at 37 °C. Completeness of starch hydrolysis to glucose was confirmed by thin layer chromatography. Since elution times for the enzymes and glucose were significantly greater than those of the PAAm, digested solutions were used without purification for size exclusion chromatography (SEC). Grafted PAAm molecular weight averages were determined by SEC using Shodex 804 and 806M columns in series with polyacrylamide standards (Polysciences). The column and detector temperatures were set at 45 °C. The mobile phase (0.1 M NaNO<sub>3</sub>) flow rate was 0.8 ml · min<sup>-1</sup>. Aliquots of the digested graft copolymer were filtered and injected without further purification. Data acquisition and analysis was performed using Chromquest (Thermo Separations) and Polymer Labs GPC Reanalysis software, respectively.

## Results and Discussion

### Monomer Content

The effect of monomer content on graft copolymer properties is shown in Table 1. Monomer content, expressed as the ratio of the acrylamide and starch feed rates (solids basis) ranged from 0.20 to 1.87. The moisture content was fixed at 50%. Average conversion at acrylamide/starch ratios of 0.77 or less was 86.6% ( $\pm 3.6\%$ ). Although conversion increased to approximately 95% at the two largest AAm/starch ratios, more data are needed to confirm the statistical significance of this increase. The conversion levels seen in Table 1 are consistent with our previous results<sup>[10]</sup> and show that persulfate is a suitable free radical initiator for reactive extrusion of starch and acrylamide.

Table 1. Effect of acrylamide/starch ratio on starch-graft-PAAm properties.<sup>a)</sup>

AAm/ starch ratio	Conversion %	Graft content %	Graft efficiency %	Solubles %	PAAm in solubles %	Mol wt ( $\times 10^{-3}$ )	Graft number $N_{AGU}$
0.20	85.0 (5.9) <sup>b)</sup>	12.3 (2.0)	74.2 (2.1)	10.0 (2.3)	39.0 (7.8)	686 (40)	15 250 (1 900)
0.33	85.8 (0.8)	19.9 (1.5)	82.0 (6.7)	10.2 (2.5)	39.8 (1.4)	936 (64)	11 600 (300)
0.48	90.4	25.8	79.0	10.8	56.6	1 056	9 400
0.62	87.9	29.0	79.2	10.4	65.8	1 075	8 100
0.77	86.3 (5.1)	31.8 (0.4)	76.4 (1.3)	13.2 (1.1)	72.3 (9.4)	995 (239)	6 600 (1 700)
1.28	97.2	41.6	59.9	25.2	82.9	1 048	4 500
1.87	94.4	45.1	52.3	32.4	85.8	1 124	4 200

<sup>a)</sup> Moisture content = 50%.<sup>b)</sup> Standard deviations for duplicate runs are in parentheses.

The effect of conversion on processing is shown by the monotonic increase in specific mechanical energy (SME) during extrusion with increasing AAm/starch ratio. SME is known to be an important parameter in extrusion processing of starch materials.<sup>[13,14]</sup> SME increases from 312 ( $\pm 6$ ) kJ  $\cdot$  kg<sup>-1</sup> to 441 ( $\pm 24$ ) kJ  $\cdot$  kg<sup>-1</sup> as the AAm/starch ratio increases from 0.20 to 1.87. This increase is consistent with the formation of polyacrylamide during extrusion, which increases the viscosity of the medium and therefore the energy required to pump it through the extruder. A similar increase in die pressure is also observed.

As expected, graft content increases with increasing AAm/starch ratio. As the concentration of monomer increases, more polyacrylamide is grafted to the starch. Grafting efficiency, defined as the amount of grafted PAAm relative to the total amount of PAAm formed, is essentially constant as AAm/starch ratio increases from 0.20 to 0.77 (78.2  $\pm$  3.0%). At the two highest AAm/starch ratios (1.28 and 1.87) grafting efficiency decreases to less than 60%. This decrease indicates that more homopolymer PAAm is formed at higher monomer contents. This is reflected in the solubles and soluble PAAm data in Table 1. As the AAm/starch ratio increases above 0.77, the amount of ethanol-water soluble material increases dramatically. The relative amount of PAAm in the soluble fraction also steadily increases with increasing AAm/starch ratio, exceeding 80% at the two highest levels. The increase in solubles shown in Table 1 is therefore due primarily to an increase in soluble PAAm.

Molecular weight of the grafted PAAm increases slightly with increasing AAm/starch ratio. An approximate plateau value of approximately 10<sup>6</sup> is seen for AAm/starch ratios greater than about 0.33.

The molecular weight distributions (MWD) of grafted PAAm samples at AAm/starch ratios of 0.20, 0.77, and 1.87 are shown in Figure 1. Samples were extracted with ethanol/water to remove ungrafted polymer, and enzyme digested to remove the starch. The chromatograms were baseline corrected and normalized relative to the peak values. Samples

at intermediate AAm/starch ratios are omitted for clarity. Common to the three MWDs is a peak at approximately 15.6 min, corresponding to a PAAm molecular weight of approximately 800 000. At AAm/starch ratios of 0.77 and 1.87, the MWDs are skewed to longer retention times (lower molecular weight) without obvious secondary peaks, suggesting a bimodal MWD. At the lowest AAm/starch ratio (0.20) the MWD displays two lower molecular peaks after the main peak at 15.6 min. These peaks correspond to molecular weights of approximately 400 000 (17.2 min) and 40 000 (19.7 min). Therefore the increase in molecular weight with AAm/starch ratio shown in Table 1 is due to the reduction in low molecular components as the monomer content increases, rather than a shift in the peak molecular weight. It is not clear why the peak molecular weight is insensitive to the effective monomer concentration; standard free radical kinetics predicts an increase in molecular weight with increasing monomer concentration.<sup>[15]</sup>

Grafting frequency is expressed as the graft number  $N_{AGU}$ , which is the average number of anhydroglucose units per PAAm graft. As seen in Table 1,  $N_{AGU}$  steadily decreases with increasing AAm/starch ratio. This decrease indicates that more graft sites are formed with increasing AAm/starch ratio, even though the efficiency of grafting decreases at the largest ratios. Larger AAm/starch ratios therefore lead to more frequent PAAm grafts of higher molecular weight. It is not clear why increasing the monomer concentration leads to increased grafting frequency. A simple chain transfer analysis<sup>[15]</sup> predicts an increase in graft number  $N_{AGU}$  with increasing AAm/starch ratio, contrary to the data in Table 1. The reduction in grafting number (increase in graft frequency) may be related the greater probability of a free radical initiated on the starch reacting with acrylamide monomer rather than oxidizing the starch. Persulfate salts are known to oxidize alcohols via a free radical mechanism<sup>[16,17]</sup> and the higher incidence of grafting may reflect a greater efficiency of polymerization initiation at higher monomer concentrations compared to oxidation reactions.

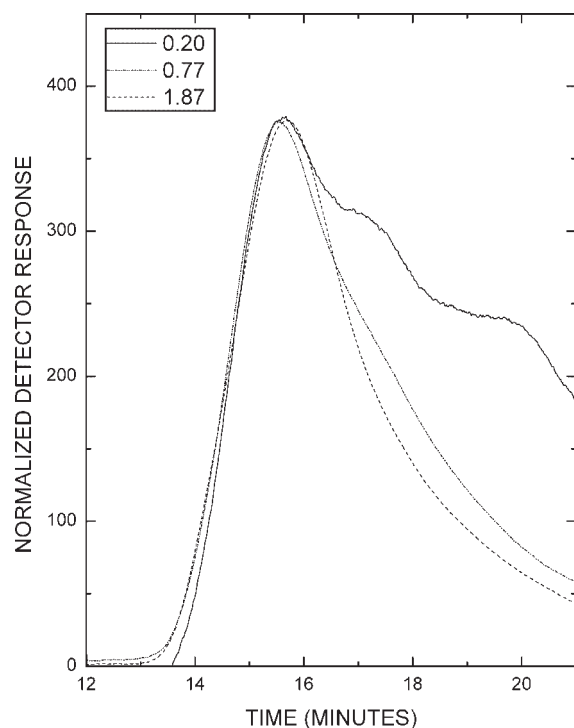


Figure 1. Molecular weight distributions of grafted polyacrylamide at different acrylamide/starch ratios: 0.20 (—), 0.77 (---), 1.87 (···).

### Moisture Content

The effect of moisture content was investigated with an AAm/starch ratio of 0.33 and a feed rate of  $180 \text{ g} \cdot \text{min}^{-1}$ . Moisture content ranged from 45 to 75%. As shown in Table 2, moisture content had a significant impact on the process characteristics and graft copolymer properties.

Conversion decreased sharply with increasing moisture content. At the lowest moisture content, conversion was 98.8%, falling to 76.8% at the highest moisture content. A similar reduction in graft content was also observed, decreasing from 24.0 to 14.1% as the moisture content increased. Graft efficiency showed a similar response to increasing moisture content, decreasing from 86.8 to 62.8%. Clearly the dilution of the reacting starch-acrylamide system has a

significant effect on the polymerization process as the solids content of the system decreases from 55 to 25%.

The amount of ethanol/water solubles increased slightly as the moisture content increased from 45 to 75%. The variance in the duplicate run at 50% moisture content suggests the increase in solubles may not be statistically significant. However, there is a clear increase in the relative amount of soluble PAAm with increasing moisture content, consistent with the formation of more soluble homopolymer PAAm.

Reducing the moisture content significantly impacted other graft copolymer properties as well. Molecular weight of grafted PAAm decreased precipitously as the moisture content increased. At the lowest moisture content, the PAAm molecular weight was just over  $10^6$ . Increasing the moisture content to 75% reduced to molecular weight by nearly an order of magnitude to 181 000. The decrease in molecular weight may be due in part to changes in the rheological properties of the system with moisture content. Specific mechanical energy (SME) increased from  $24 (\pm 2) \text{ kJ} \cdot \text{kg}^{-1}$  at 75% moisture content to  $558 (\pm 27) \text{ kJ} \cdot \text{kg}^{-1}$  at 45% moisture content, consistent with lower viscosity at higher moisture content. Higher molecular weights are consistent with a reduced rate of chain termination in a higher viscosity fluid, similar to the Trommsdorf effect.<sup>[15]</sup>

Molecular weight distributions of grafted PAAm are significantly affected by moisture content, as shown in Figure 2. The molecular weight distributions are all clearly bimodal (the 50% moisture content data are omitted for clarity). The peak at  $\approx 21 \text{ min}$  in each curve is due to the enzyme used for starch digestion. The peak at approximately 16 min corresponds to a molecular weight of approximately 500 000 while the peak at 18 min corresponds to a molecular weight of approximately 100 000. At the highest moisture content, the lower molecular weight component is dominant. As the moisture content decreases, the relative height of the higher molecular component increases and shifts to slightly shorter elution times (16.7 min at 75% moisture content to 16.2 min at 45% moisture content). The lower molecular weight peak also shifts to shorter elution times as the moisture content decreases. In addition, the onset time for each MWD shifts to shorter

Table 2. Effect of moisture content on starch-graft-PAAm properties.<sup>a)</sup>

Moisture content	Conversion	Graft content	Graft efficiency	Solubles	PAAm in solubles	Mol wt ( $\times 10^{-3}$ )	Graft number $N_{\text{AGU}}$
%	%	%	%	%	%		
75	76.8	14.1	62.8	14.0	53.9	181	3 400
65	86.4	18.5	79.0	8.8	58.0	407	5 500
55	88.9	20.3	81.9	8.0	45.5	852	10 300
50 <sup>b)</sup>	85.8 (0.8)	19.9 (1.5)	82.0 (6.7)	10.2 (2.5)	39.8 (1.4)	936 (64)	11 600 (300)
45	98.8	24.0	86.8	9.2	38.3	1 020	10 000

<sup>a)</sup> Acrylamide/starch ratio = 0.33.

<sup>b)</sup> Standard deviations for duplicate runs are in parentheses.



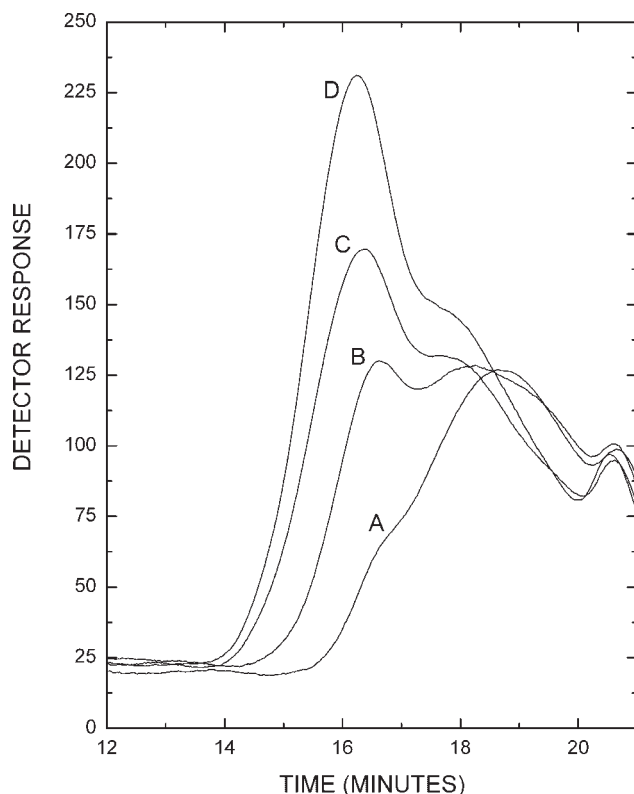


Figure 2. Molecular weight distributions of grafted polyacrylamide at different moisture contents during extrusion: A) 75%; B) 65%; C) 55%; D) 45%.

elution times as the moisture content decreases, consistent with the formation of higher molecular weight PAAm at lower moisture content. The source of the bimodal nature of the MWDs is not obvious, but it does not appear to be related to the dual injection scheme used for the persulfate initiator (unpublished results).

The graft number  $N_{AGU}$  decreases with increasing moisture content, giving more grafts of lower molecular weight. A similar dilution effect was observed by Fanta et al.<sup>[18,19]</sup> in batch preparations of starch-polyacrylonitrile graft copolymers using ceric ammonium nitrate.

## Conclusion

We have shown that monomer/starch ratio and moisture content have significant impact of the properties of starch-polyacrylamide graft copolymers prepared by reactive extrusion. Increasing the acrylamide/starch ratio leads to graft copolymers with more grafts of higher molecular weight, even as the graft efficiency decreases. Increasing moisture content gives more grafts of lower molecular

weight, as well as decreased conversion and graft efficiency. These results demonstrate that graft copolymer properties can be controlled by selection of acrylamide/starch ratio and moisture contents during reactive extrusion.

## Disclaimer

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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